SHIMADZU
Excellence in Science

Technical Report

Simultaneous positive and negative HRAM acquisition using a Q-TOF mass spectrometer with ultra-high mass stability

Tomoyuki Oshiro[1], Yuta Miyazaki[1], Tsuyoshi Nakanishi[1], Atsuhiko Toyama[1], Daisuke Okumura[1]

Abstract:

To enable simultaneous positive and negative ion mode MS acquisition on a Q-TOF system, we developed a novel conversion equation for calculating *m/z* from the measured TOF that compensates for the high-voltage instability after polarity switching. By applying this algorithm to Shimadzu LCMS-9050, it was demonstrated that 600 msec polarity switching time was sufficient for simultaneously achieving low-ppm mass accuracies in both positive and negative modes.

Keywords: LCMS-9050, Q-TOF, polarity switching, mass stability, mass accuracy

1. Introduction

Quadrupole time-of-flight mass spectrometers (Q-TOF) are a powerful and robust tool for high-resolution accurate-mass (HRAM) data acquisition. However, even though Q-TOF can run in both positive and negative ion modes, it is widely considered impractical to run the two modes in a single LC-MS analysis.
Polarity switching typically results in a considerable compromise in the accuracy of measured masses, observed as a mass shift that continues for hours after polarity switching. The cause of this phenomenon is the instability of high voltages (several kV) applied to TOF components, which occurs as a result of shifting the voltage across a large amplitude during the switching event. We introduce a new system that mitigates the above issue.

2. Concept

In a time-of-flight mass spectrometer, the relationship between the time-of-flight "t" and the mass to charge ratio "*m/z*" is commonly employed [Equation A].

$$E = qV = zeV = \frac{1}{2}mv^2$$

$$t = a\sqrt{m/_z} + b \qquad \text{[A]}$$

Note:
E : Energy of the ion
q : charge of the ion
V : potential of the ion
e : elementary charge
z : valence of the ion
m : mass of the ion
v : velocity of the ion
a, b : constant parameters

This equation assumes that the high voltage applied to the TOF system is constant. However, this is far from the reality when polarity switching takes place. The polarity switching time (Fig. 2) depends on stray capacity of metal parts such as flight tube or ion reflector and characteristics of power source, and it typically takes several seconds to fully stabilize the power source voltage.

Fig. 1 Shimadzu LCMS-9050 was used for this investigation.

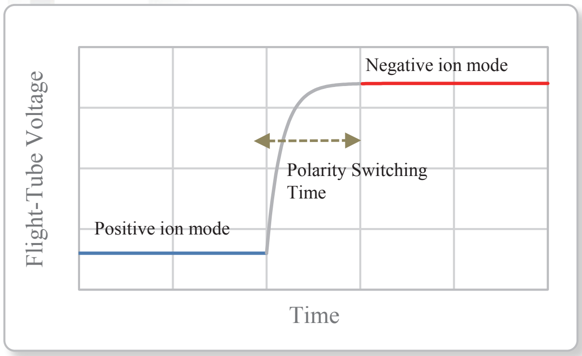

Fig. 2 The technical barrier to fast polarity switching. Seconds of polarity switching times are required to achieve high mass accuracy after polarity switching.

To shorten the effective polarity switching time, we introduced a new term representing the time elapsed after the polarity switching was initiated to [Equation A].
The correction term was expressed as function "$f\,(t_p,\ t_a)$" where "t_p" is the elapsed time after the polarity switching and "t_a" is the data acquisition time (Fig. 3).
Equations for "t" and "*m/z*" including the correction terms "$f\,(t_p,\ t_a)$" are given in [Equation B].

---

[1] Analytical & Measuring Instruments Division

$$t = \left(a - f(t_p, t_a)\right) \cdot \sqrt{m/z} + b \qquad [B]$$

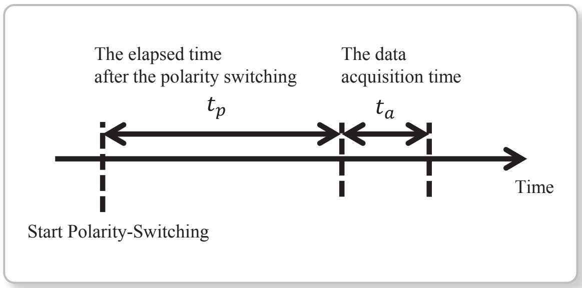

Fig. 3 A schematic diagram showing the concepts of t_p, t_a.

3. Result

As the reference data, TOF spectra were acquired at 100 msec intervals starting from 500 msec after the polarity switching sequence was initiated. The accuracies of *m/z* converted by [Equation A] were plotted (Fig. 4, blue trace). The data showed that the mass accuracy was stable at 1 sec after the start of polarity switching. This was considered the best-effort performance by the HV power supply alone.

Using the reference data, the parameter of the correction term was decided, and an additional set of TOF data was converted to *m/z* by [Equation B] (Fig. 4, red trace). The correction term resulted in a dramatic improvement in the mass accuracies at short polarity switching times.

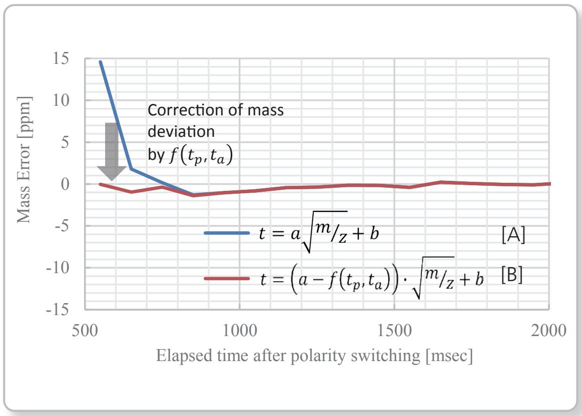

Fig. 4 Results of mass accuracy measurement.
The measured mass is sodium iodide $[NaI]_6Na^+$ (theorical *m/z* is 922.3547), the standard sample of Shimadzu Q-TOF.

Moreover, as summarized in Table 1, we observed that introduction of the correction term was effective over a wide *m/z* range for the polarity switching time of 600 msec. The mass errors observed were less than 1 ppm in the positive mode and less than 3 ppm in the negative mode.

Table 1 Mass error measurement results of sodium iodide during simultaneous positive and negative ion measurements at t_p=600 ms and t_a=50 ms

Positive-ion	$[NaI]Na^+$	$[NaI]_3Na^+$	$[NaI]_6Na^+$	$[NaI]_{10}Na^+$	$[NaI]_{13}Na^+$
m/z	172.8834	472.6727	922.3562	1521.9337	1971.6166
Mass Error [ppm]	-0.87	-0.53	-0.60	-0.54	-0.67

Positive-ion	$[NaI]I^-$	$[NaI]_2I^-$	$[NaI]_4I^-$	$[NaI]_6I^-$	$[NaI]_{10}I^-$
m/z	276.8004	426.6950	726.4849	1026.2748	1625.8538
Mass Error [ppm]	2.02	2.15	2.4	2.03	2.67

Robustness of simultaneous positive and negative acquisition was tested by monitoring the mass errors over 24 hours without re-calibration. For the set of antibiotic standards (MW 150-1100 Da), the observed mass errors were within 3 ppm throughout under the real laboratory condition. (Fig.5)

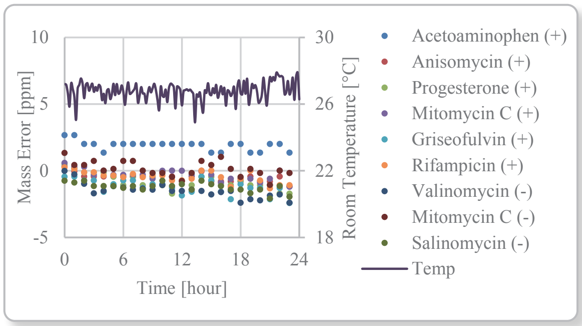

Fig. 5 Results of long-term mass accuracy measurement.

4. Conclusion

The calibration algorithm implemented in LCMS-9050 successfully compensates for the high-voltage instability and achieves low-ppm mass accuracy for an analysis with polarity switching. This makes a simultaneous positive and negative acquisition a viable option for HRAM analysis, thereby increasing the analytical throughput by two-fold compared to running two analyses for positive and negative.

SHIMADZU

Shimadzu Corporation
www.shimadzu.com/an/